

**METHOD FOR MAKING A HIGH TEMPERATURE EROSION RESISTANT  
MATERIAL CONTAINING COMPACTED HOLLOW GEOMETRIC SHAPES**

*Fig. A'*

**BACKGROUND OF THE INVENTION**

**Field of the Invention**

5                   The present invention relates to a method of making high temperature, erosion resistant materials that are used in high temperature environments.

**Background Information**

10                   Most components of combustion turbines are operated at very high temperatures and often require the use of specialized coatings/inserts to protect underlying supporting materials. These specialized coating/inserts include thermal barrier coatings (TBCs), turbine blade tip inserts, and abradable seals disposed opposite the turbine blade tips.

15                   Conventional TBCs typically comprise a thin layer of a ceramic material covering an alloy. In many applications, the coatings must be resistant to extremely high temperature, erosion resistant. These materials may also be used as an abradable material. An example of an abradable material is turbine ring seal segments, which fit with tight tolerances against the tips of turbine blades, must withstand erosion and must preferentially wear or abrade in order to reduce damage to the turbine blades, and form a tight seal with the turbine blade. Protective coating system can include several layers including a metallic bond  
20                   or barrier coating of MCrAlY having an alumina scale and, for example, a columnar yttria stabilized zirconia thermal barrier, which can be further coated by an erosion resistant layer of alumina or silicon carbide, applied by physical vapor deposition techniques.

25                   Fillers have also been used. There, abradable stationary seal walls, for jet turbine housings which seal opposing, rotating rotor blade tips, have a ceramic core containing from 30 vol. % to 98 vol. % solid ceramic filler, where the ceramic fills a honeycomb wall structure. This is then covered with erosion and corrosion resistant outer layer, which is made porous by uniformly dispersed, finely divided filler. This is apparently applied by a spraying technique. The pores can be filled with ceramic, metal oxide or

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carbide materials. Fillers mentioned include hollow  $\text{ZrO}_2 \cdot 8\text{YO}_3$  ceramic spheres and solid  $\text{Al}_2\text{O}_3$ , SiC, TiC and BN spheres.

Other abradable honeycomb structures have been developed for use in turbines. Low melting fluorides, such as  $\text{BaF}_2$ , are incorporated into a stabilized zirconia or alumina matrix which, in turn, is used to fill a honeycomb shroud lining made of, for example, a metal alloy. The filling becomes molten when the rotating blade tips rub the shroud, and upon resolidification, improve the smoothness of the abraded surface. Another variation of reinforced ceramic layers, including a honeycomb matrix for use in a turbine as abradable seals.

Also, U.S. patent No. 6,013,592 which is referenced here and is incorporated herein in its entirety, teaches a material containing hollow ceramic particles embedded in an interconnected ceramic matrix, to provide a composite thermal barrier coating system having superior erosion resistance and abrasion properties for use on combustion turbine components. The hollow particles were preferably spherical and made of zirconia, alumina, mullite, ceria, YAG or the like, having an average particle size of about 200 micrometers (0.2 mm) to 1500 micrometers (1.5 mm). The steady state erosion rate, (grams lost/kg of erosive impacting media or g/kg), of this filler was 3.2 g/kg vs. 4.6 to 8.6 g/kg for conventional TBCs.

The present invention is a method of forming an insulating material. And more specifically for forming the insulating material into larger three dimensional geometric shapes, such as cylinders. Here, the insulating material is formed by providing a permeable structure that has a contacting surface. A fibrous material is placed against the contacting surface of the permeable structure and then the hollow ceramic spheres are placed against the fibrous material. A slurry mixture containing a binder and filler particles is either poured directly into the space containing the hollow spheres, or into a space adjacent to the hollow spheres. Then, pressure is applied such that the slurry passes around the hollow spheres filling in any voids between the spheres and such that the slurry is also forced against the fibrous material. This fibrous material allows capillary wicking of the liquid in the slurry thereby permitting the filler particles to fill the void spaces between the spheres. The fibrous

material also allows controlled removal of the liquid in the slurry and allows controlled partial drying of the sphere and slurry casting. This insulating material casting is then further heat dried then fired to create a ceramic matrix material that is highly resistive to erosion and has a very low thermal conductivity.

5 U.S. Patent Application Serial No. 09/267,237 (Merrill et al., filed on December 20, 1999) described a material useful as an erosion resistant layer for turbine applications. There, closely packed hollow, geometric shapes, such as hollow spheres were mixed with binder and filler particles, cast into a mold, dried and then fired to provide abradable, porous, thermally stable seals, and the like. This system works well for making  
10 flat structures.

The present invention has been developed as an improved process of forming larger three dimensional geometric shapes, in view of the foregoing, and to address other deficiencies of the prior art. Therefore, it is one of the main objects of this invention to provide a method making a high temperature, erosion resistant coating and material which is  
15 non-shrinking, thermally insulating, in larger geometric shapes and thermally stable up to at least 1600°C, and which has constrained stabilized porosity and insulating properties, as well as controlled thermal conductivity and thermal expansion properties.

#### SUMMARY OF THE INVENTION

These and other objects of the invention are accomplished by providing  
20 method of making an insulating material, useful as an erosion resistant high temperature layer, for large geometric shapes comprising the steps of providing a first permeable structure having a contacting surface, and a second structure which may or may not be permeable depending on the size and geometry of the part. As the part size increases, the second structure is more likely to be permeable. These first and second structures define a  
25 void space for both an extractable fibrous insulation member and for the hollow spheres. Hollow ceramic spheres are placed in the sphere chamber against the contacting surface, poring a slurry against the hollow spheres, and applying pressure such the slurry passes around the hollow spheres filling in any voids adjacent the spheres and being forced against the contacting surface.

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Next, an extracting member of fibrous material is located against the contacting surface of the first permeable structure. This extracting member, in combination with the two structures noted above, defines the geometry of the void space or sphere chamber which is filled by the hollow ceramic spheres and slurry and which facilitates the drying of the insulating material by allowing capillary wicking of the liquid from the slurry around the spheres thus partially drying the resulting insulating material structure. The partially dried material is then further dried and fired for use as a thermal barrier .

Preferably, the geometric shapes are selected from rigid, hollow, essentially closed ceramic spheres and other similar geometric shapes of low aspect ratio, less than 10 and preferably less than 5, such as hollow cylinders and the like. The shapes are "individually formed," defined here as formed separately and stabilized, rather than being formed *in situ* on a substrate etc. The hollow ceramic shapes have "dense" walls, defined here as having a density from 90% to 100% of theoretical (0% to 10% porous). Because the geometric shapes are independently formed and fired at temperatures above their intended use temperature, dense wall formation occurs and a non-sinterable rigid shape results, which allows crack deflection and general toughening of the material, as well as allowing stabilization to very high temperatures approaching 1700°C. If needed, void spaces between the larger hollow geometric shapes can be filled with smaller diameter hollow geometric shapes, to reduce void volume.

Preferably, there are three dimensional close packed structures of hollow shapes, that can be any geometry, such as, spheres, cylinders, ovoids, etc. This close packed structure provides strength, a nonsinterable stable structure, and a mostly isotropic material and it also minimizes large void spaces and provides a uniform macro- and micro-porosity distribution within the sphere. The material should have some measure of porosity, at least 15 vol. % but preferably between 40 vol. % to 70 vol. % for turbine thermal insulating and abradable coatings.

The method of this invention allows such porous shapes having close packed structures which, when sintered, can be either friable and/or erosion resistant depending on the processing parameters (such as sphere size, wall thickness, composition, etc) while

maintaining a low elastic modulus when formed into large or complex three dimensional geometric shapes, such as a combustion liners or vane airfoil for combustion turbine engines.

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### BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further illustrated by the following non-limiting drawings, in which:

FIG. 1 is a cross-section of the apparatus to perform the methods of the present invention.

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FIG. 2 is an magnified view of the apparatus used for the method of the present invention.

FIG. 3 is the thermal insulating material of the present invention cast into a large geometric shape, a cylinder.

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### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

sub Aa Referring to FIG 1 and 2 there is shown the mold apparatus used for the method of the present invention. The mold apparatus 8 includes a first permeable wall structure 10, a extracting fibrous material 12, a second permeable wall 14 and a impermeable wall 16. The permeable wall 10 and 14 along with the impermeable wall 16 are closed on the ends to define voids between the walls 10, 14, and 16 or chambers 24, and 30 there between. Openings 18 and 20 are provided as an entry point into the chambers 24 and 30. The function of each of these elements in accordance with the present invention will be discussed in more detail hereafter.

The method of the present invention begins with filling the chamber 30 with geometric shapes 26 such as spheres which are preferably hollow. The geometric shapes 26 are preferably compacted by vibrating the mold 8 or by other means to insure that the voids or spaces between each geometric shapes or spheres 26 are minimized.

Referring to both figures 1 and 2, most spheres 26 contact at least two other spheres 26, with a substantial number, that is about 70 % contacting three other spheres 26.

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The voids or spaces 28 between the spheres 26 provide a moderate porosity to allow a slurry to pass around the spheres 26.

Now focusing on the characteristics of the spheres 26, the erosion performance of the present inventions resulting insulating material 22 is achieved through the use of dense-walled geometric shapes which are resistant to small particle erosion. Abradability is likewise achieved through the introduction of coarse geometric shapes with (more than 100 microns) closed porosity. The simultaneous optimization of both erosion resistance and abradability is achieved through judicious selection of the values and scale of closed porosity, hollow sphere size and wall thickness. The contribution of the spaces 28 that are filled with a slurry comprised of a binder and filler material is primarily in the mechanical integrity of the structure (strength and elastic constants). The filler material occupies the void spaces 28 and the binder coats both the filler material and the spheres and can also fill small void spaces between the filler material particles and the spheres. During firing, the binder sinters together the filler and sphere materials to provide a rigid structure.

The method of the present invention has almost universal chain formation in three dimensions of the spheres 26, i.e. a uniform isotropic close-packed structure, providing a high level of constrained stabilized uniform spherical porosity. That is, the chains prevent collapse and shrinking of the insulating material 22 at temperatures approaching 1700°C. It is easy to see how the present invention's 50 vol. % to 90 vol. % hollow shape, here hollow sphere configuration, allows minimizing the void spaces 28. Providing an array, as closely packed as that shown in FIGS 1 and 2, where the void spaces 28 are essentially filled by the slurry, requires a specialized method of packing and impregnation, as will be discussed in detailed hereafter. The hollow geometric shapes are "substantially close packed" meaning that the array is as shown in the type array shown in FIGS. 1 and 2, where the coordination number, is greater than or equal to 1.

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More specifically referring now to FIG. 2, which more clearly illustrates the method of this invention, the spheres 26, are preferable hollow ceramic spheres having walls, which are shown. Optionally, smaller hollow shapes, such as hollow spheres, as well as the slurry can be used to fill void space 28 between the hollow spheres 26. The hollow ceramic

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spheres 26 are manufactured such that the sphere walls are near 70% to 100% of theoretical density, preferably near 90% to 100% of theoretical density (10% to 0% porous). For good erosion resistance, the wall thickness is preferably between about 100 micrometers to 400 micrometers, depending on sphere diameter. The hollow ceramic spheres 26 are non-sinterable objects which uniquely control the dimensional stability of the material 22 and inhibit volumetric shrinkage during sintering of the resulting insulating material 22. The hollow spheres 26 are also critical in establishing the unique macro- and microstructure of the material 22 and in controlling its unique behavior, both thermally and mechanically. The level of closed macroscopic porosity within the material 22 is defined by the overall size of the hollow ceramic spheres, the wall thickness of the spheres, and their packing arrangement within the structure. The binder material that interstitially bonds or sinters the hollow ceramic spheres together during firing may also contribute a secondary role to these properties depending on the mechanical and thermal properties and the amount of binder materials used. The structure of the resulting material 22 into large geometric shapes such as a cylinder 32, as shown in Figure 3, in accordance with the method of the present invention, imparts unique combinations of properties including, for gas turbine applications, excellent erosion resistance, insulating properties, for components such as combustors and the like and may also be used where abrasability is needed which is not achieved by conventional means.

As stated above, the resulting material 22, using the method of the present invention, has closed macroscopic porosity, via the use of hollow ceramic spheres 26 (or similar geometric shapes) of size ranges between 150 micrometers diameter to 5000 micrometers diameter, which are independently formed and subsequently bonded together to form a macroscopic infrastructure. The bulk density of these spheres 26 themselves is anywhere between 0.1 and 0.9 of theoretical, that is 10% to 90% of theoretical density, taking into account the internal porosity, and depending upon the needs for each high temperature application. The close-packed, contiguous structure defines and controls the thermal and mechanical properties of the material 22 and maintains dimensional stability of the material 22 as a thermal insulating layer. Coordination numbers for the sphere packing can range from 1 to 14, but preferably, the coordination number of substantially all of the

hollow shapes is from 5 to 12, and even more ideally from 5 to 8 for gas turbine coating applications. Some degree of randomness in the coordination number may be desired depending upon the application strength, toughness, abrasability and erosion resistance requirements.. However, idealized packing arrangements and high coordination numbers in the 8 to 14 range, may be preferred for stiffness-driven applications such as cores for sandwich structures.

It is critical that the spheres 26 be separately formed and stabilized and then used as such in this method vs. their being formed in-situ. The individually formed and bonded spheres impart unique properties to the resulting material 22 Forming the spheres separately allows the stabilization of the spheres to a much higher temperature than otherwise possible. This tailored pore structure is in contrast to the other coating methods where in-situ formed voids are generally interconnected, thus increasing the overall size of critical defects and weakening the structure, the present invention does not produce interconnected void networks thus making it a stronger more stabilized material.

The ceramic hollow spheres 26 will typically have a wall thickness-to-radius ratio ("t/r" ratio) of between 0.05 to 0.50. Depending upon the application, this "t/r" ratio can vary, for example: for lightweight insulation material where erosion is not critical (or is accommodated), t/r in the lower end of this range is desirable; for insulating or abrasable coatings, that is, in a gas turbine, where erosion is a concern, t/r between 0.1 – 0.4 is preferable; for very strong or more erosion resistant materials, the higher end of the t/r range is desirable.

For many applications, the absolute value of the wall thickness is critical to achieving adequate erosion resistance. Therefore, the t/r and overall diameter of the spheres must be considered. For example, if a 200 micrometer wall thickness is required for erosion resistance, and the overall bulk density of the material 22 is defined by abrasability requirements, that is, about 60%, this helps narrow down the range of sphere sizes possible (other variables include sphere packing density and matrix density). Wall thickness will generally range from about 0.05 mm (50 micrometers) to 5.0 mm (500 micrometers).



The shape of the hollow particles 26 is ideally spherical, for ease of manufacture and for attaining isotropic properties. However, other similar shapes can be readily made and incorporated in like manner and perhaps introduce certain optimized properties, for example, the shapes can be hollow elongated spheroids or needlelike shapes either randomly oriented or preferentially oriented parallel or perpendicular to the substrate surface and having aspect ratios less than 5-to-1 and lengths between 150 micrometers and 5000 micrometers. Hollow ellipses or other irregular spheroids can be made and indeed are within the normal range of sphere manufacture. Mixtures of spheres, spheroids, low aspect ratio cylinders and other shapes are also natural extensions for use in the method of this invention and, in fact, at least one manufacturing process for hollow spheres also produces hollow, long needle structures. While the invention involves a method of making a insulating material 22, it is important to recognize the unique properties and parameters of that system, which are accomplished by the manufacturing techniques which will be detailed shortly.

Overall bulk density of the entire material 22 made using the method of this invention, including the sphere density, their packing arrangement, and the filler/binder slurry or matrix material is generally in the range of 0.10 to 0.80 of theoretical density, depending on the application. For the example of turbine engine coatings for either insulation or abrasability (or both), the range of overall density of the material 22 and its makeup can vary over a wide range. By controlling the bulk density, that is, sphere size, sphere wall thickness and matrix, the matrix comprises both the binder and filler materials, density) of the material 22, the properties can be optimized for erosion resistance and/or abrasability. The best range for abrasable coatings is 30% to 80% theoretical density. The best range for erosion resistance is from about a 0.3 to 0.5 t/r within the 30% to 80% range.

Note that while FIGS. 1 and 2 show cases of regular packing of uniformly sized spheres 26, the packing of the spheres is not limited to either form or packing nor is it limited to uniformly sized spheres, nor is it limited to any kind of regularity of structure (random packing is more the norm and is allowable so long as the at least substantially

“close-packing” criteria is met). Non-uniform sphere sizing may be desirable to achieve higher sphere packing densities while maintaining randomness of the structure.

Sphere walls must be over 70% dense, but are preferably near theoretical density (90% to 100% of theoretical density) to maintain thermal stability over the widest range of temperatures. The high density of the sphere walls imparts excellent erosion resistance and controls the thermal and mechanical behavior of the material 22. The manufacturing temperature of the hollow spheres is well in excess of the intended use temperature of the material 22, for example, mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) hollow spheres can be manufactured at  $1750^\circ\text{C}$ , rendering them inert and stable in a material 22 operating indefinitely at  $1600^\circ\text{C}$  to  $1700^\circ\text{C}$ . Separately forming and stabilizing the spheres to high temperatures ensures the thermal and dimensional stability of the resulting material 22 of the present invention method at future high temperature operating ranges up to  $1700^\circ\text{C}$  and possibly beyond.

The hollow ceramic spheres, 26 rods, etc. are bonded together interstitially by a ceramic matrix's binder material to form a contiguous and self-supporting structure. The matrix material itself begins as a slurry that is flowable around the spheres 26 with the resulting interconnected network of spheres, filler particles in void spaces and the binder material forming contiguous structures of the resulting material 22. The matrix material is the resulting phases of the binder and filler materials which form during sintering; typically the filler does not change phase but the binder may go through several phase changes during the firing process. The binder material can be a chemical solution, a polymeric or colloidal sol, a very active fine powder dispersed in a fluid medium, etc. A key property of the binder is that it is an active readily sintereable material, whereas, both the spheres and the filler materials are typically inactive mostly nonsinterable materials. The volume content of the matrix material can vary from near zero to completely filling in the interstitial space between the hollow shapes. Preferably the matrix constitutes a minimum of 10% of the interstitial space between the hollow shapes for all coordination members. The binder content and final density are tailored to achieve the desired properties for the specific application, taking into account: the desired bond strength between hollow shapes; the overall bulk density required

5           The binder may or may not contain filler or reinforcing media, including but not limited to, smaller hollow spheres or other geometric shapes, powders, particles, platelets, and whiskers or chopped fibers or other discontinuous fibrous materials. In the case of thick-walled shapes where  $t/r$  is greater than 0.25, it may be advantageous to minimize the amount of matrix in the system – so long as the bond strength and other criteria are met. A very strong structure, particularly in compression, can be achieved with very little matrix addition.

### TABLE 1

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Typically, high temperature, stable ceramic particulate materials are used for the fillers in the matrix system for the material 22. The purpose of these fillers may be to add density to the matrix (without necessarily adding strength), add strength to the matrix, add toughness to the matrix, either via reinforcing or residual stress management, or improve the volumetric yield of matrix infiltrates (cost savings). Preferably the matrix slurry based binder mixture is mullite and mono-aluminum phosphate solution but they can also be, composition but not limited to those in Table 2 below, and typical binders are listed in Table 3 below.

TABLE 3

PARTICULATE		BINDER
Mullite	with	Aluminosilicate/Aluminumphosphate
Alumina	with	Aluminumphosphate/ Aluminumoxychloride
Zirconia	with	Aluminumorthophosphate
Hafnia	with	Aluminumorthophosphate
Yttria	with	Aluminumorthophosphate
Yttrium Aluminum Garnet (YAG)	with	Aluminumorthophosphate
Ceria	with	Aluminumorthophosphate
Silicon Carbide or Silicon Nitride	with	Polycarbosilane
Hollow Shapes of the Above	with	All Binders Listed Above

These materials are slowly mixed together, usually with deionized water, to allow good dispersion to form the slurry. In some cases an acid, such as nitric acid, may be added to maintain the pH of the slurry infiltration solution in the range of approximately 3 to 4.

5 In the method of the present invention, the slurry chamber 24, is provided to initially contain slurry. The slurry is poured into the slurry chamber 24 through opening 20. As stated above the spheres 26 are in place in sphere chamber 30, in a close packed array. The porous membrane 14 is used to define one side of the sphere chamber 30. The porous membrane 14 may be any suitable membrane or sheet of material having perforations  
10 therein. For example the membrane 14 can be a sheet of stainless steel having perforation therein, with the perforation having a diameter of 1.5mm and spaced apart 3mm between each perforation hole center. This diameter of the perforations are smaller than the diameter of the spheres 26 but larger enough to allow the slurry mixture to pass there through.

The fibrous material 12 defines the other side of the sphere chamber 30. This  
15 fibrous material allows the liquid of the slurry to pass through, but does not allow the filler to  
pass through. The permeable structure 10 provides for easy separation is plastic based, is  
typically less than 0.5mm thick and can be removed easily after infiltration or during partial  
firing of the entire assembly. A filter maybe used against the fibrous material for easy  
release for the insulating material from the fibrous material . The filter is typically made of  
20 paper and less than 0.25mm thick that will and will burn away during the firing process  
leaving no residue.

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The material 22 can be heated to about 120°C to further drying the material 22. After the extracting membrane is removed, it can be further heated, in steps of 2°C to 10°C per minute, to 1000°C, to form a secure, unitary structure. To form a true refractory

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version, the body can be fired by further heating, in steps of 3°C to 10°C per minute, to about 1600°C and held for approximately four to ten hours.

The method of this invention goes beyond phosphate bonding of ceramic hollow spheres using aluminum phosphate and controlled capillary drying of slurry based components to make three-dimensional type layers that could be bonded to a substrate having the same three dimensional shape. This invention is projected for use in complex 3D components such as vane airfoils and combustor liners. This invention provides for the application to complex 3D shapes because it employs alternate binders to bond together the ceramic spheres and filler powders. Specifically, the processing is not based on capillary drying but is rather based on a process of impregnation, preferably under pressure. The mold forms used can be of any required shape, which means that complex shape forms of these coatings can be produced. This process is more controllable and can also be tailored to provide different coating structures to suit requirements such as erosion resistance and abrasability.

A number of liquid binder solutions can be used to form effective binding of the system. These include monoaluminum phosphate, aluminum hydroxyl chloride and ceramic sols that generate alumina, silica, yttria or zirconia solids. All of these binders dictate different and specific firing schedules.

Other applications for the material of this invention may include making materials for application as combustor liners (can, annular, and can-annular configurations), transition ducts, static airfoils and platforms (vanes), seals (both blade tip and interstage), and virtually any static surface exposed to a hot gas path. Aerospace applications include aircraft hot gas (engine exhaust) impinged structures and surfaces; thermal protection systems (TPS) for aerospace vehicles (hypersonic or re-entry protection); stiff, lightweight panels or structures for space systems (satellites, vehicles, stations, etc.), etc. Diesel or other ICE applications include cylinder liners, exhaust ports, header liners, etc.

The present invention may be embodied in other forms without departing from the spirit or essential attributes thereof, and accordingly, reference should be made to

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both the appended claims and the foregoing specification as indicating the scope of the invention.

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